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T.A. Wheat
Ceramic Section
Mineral Processing Laboratory

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THE CANMET PROGRAM TO DEVELOP SOLID ELECTROLYTES

by

T.A. Wheat*

ABSTRACT

A brief review is given of the current CANMET program in FY 1982/83 for the R & D of selected solid electrolytes that have potential application in various energy storage and conversion systems.

The program encompasses work conducted in universities and industry under contract as well as that performed internally in the CANMET laboratories.

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*Research Scientist, Ceramics Section, Mineral Processing Laboratory, Mineral Sciences Laboratories, CANMET, Energy, Mines and Resources Canada, Ottawa.

INTRODUCTION

The purpose of the present report is to revise information given previously in early 1981 (ERP/MSL 81-11 (TR)). Hence, it is assumed that the reader is familiar with the background to this field and the various potentially important applications for the increasingly wide range of solid-state electrolytes that are under development in many countries.

The objective of the present CANMET program is to develop those electrolytes that are candidates for use in high energy-density batteries (such as those based on the Na-S cell), thermo-electric generators (based on recirculating Na), fuel cells and vapour-phase electrolyzers. Broadly, that implies that attention will be given to those stable materials conductive to the Group IA elements - particularly H, Li and Na. In addition, because of their significance to the closed-loop control of conventional combustion equipment, attention has also been given to the range of oxygen conductors.

CURRENT R & D

The CANMET program is divided into several areas - all of which are focussed on materials development at present. In its essence, the present program reflects the progressive evolution of the development and exploitation of solid electrolytes in CANMET and the transfer of the potentially important areas of technology to Canadian industry.

Two projects exist in CANMET dealing with the development of solid electrolytes (450201 - Electrical Energy Storage Devices; 450203 - Hydrogen-Air Fuel Cell), and there is a considerable degree of interaction between the two. For example, the formation of a solid proton-conducting electrolyte depends on the room-temperature ion-exchange of sintered bars of K beta"-alumina, which is examined under the first project, whereas the properties of the ion-exchanged product are studied under the second project. Because of this inter-relationship, the work below is reported on a materials and processing technology basis rather than strictly on project lines.

Oxygen Conductors

Currently a number of oxygen-ion conducting solids are under extensive development in various centres. Among the more prominent families are

those having either a fluorite, perovskite or pyrochlore structure. Of these, the fluorites are the most common and they include the doped zirconias, cerias and delta-bismuth oxide (1).

Because of the attractive engineering properties of the partially stabilized zirconia-based alloys, such as their extremely high thermal shock resistance and moderately high fracture toughness, this group of materials are under active development in a number of laboratories (2,3). However, there is little information available on the changes that can be expected to occur in the dielectric properties as a function of the composition, temperature and thermal history. For that reason, the thermal conductivity and diffusivity of a range of calcia-stabilized alloys having up to 22.2 mol% CaO are under study. As the applications for these materials (such as sensors and fuel cells) require high-temperature operation, the effect of thermal cycling is of special interest.

Hydrogen Conductors

The development of this potentially important group of solid electrolytes was first included in the CANMET program in 1979, but, because of staffing difficulties in 1980 and 1981, no R & D was conducted in CANMET during that period. However, during the period 1976-1980, CANMET had a program to develop the sodium-conducting beta- and beta"-aluminas (the latter is the more desirable as it has approximately three times the conductivity). During that time, the technology was successfully transferred to McMaster University (1977), Almax Industries Ltd. (1978) and Queen's University (1980).

By late 1978, the first report of hydrogen-ion conduction in both beta- and beta"-alumina had been made by researchers (4,5). Consequently, supported by NRC funding, a joint program was initiated between the universities of McMaster and Queen's with CANMET as technical consultants to develop the hydrogen-conducting form of a beta"-alumina because it was speculated by analogy with the sodium-ion conducting forms that a significantly higher hydrogen-ion conductivity should be exhibited by the beta" phase.

As a result of two years experience using CANMET technology to initially produce high-quality sodium beta"-aluminas, the development of a hydrogen-conducting analogue was completed on a small scale within a year and patent application covering the process was filed on behalf of the Crown in April, 1980. As a result of this successful adaptation of the original CANMET

technology, a proposal was made to the National Energy Program in early 1981 to develop the technology further and exploit it in a novel hydrogen-air fuel cell. Partial support for this proposal was received in September, 1981.

In FY's 1982/84, the work will focus on developing a more industrially acceptable process for the production of the basic electrolyte. Thereafter, the overall performance and durability of the beta-alumina electrolyte will be established under operating conditions, where noble-metal electrodes will be used initially. The program will also examine the possibility of using non-noble metals and also ceramics as suitable electrode materials (possibilities include the appropriate analogues of selected mixed conductors such as ion-exchanged sintered porous ferrites and tungsten bronzes). However, even if the system demands the use of noble metals, the cost is not expected to be a barrier to commercial development - for the past few years the modern automobile has used a catalytic convertor containing ~3 g of Pt as part of the emission-control system.

Up to present, the production of a hydrogen-conducting solid electrolyte has been limited to the use of a spray-freezing and freeze-drying process as it is capable of producing essentially atomically mixed, highly reactive precursor materials. However, the process is slow and unsuitable for industrial purposes and hence the emphasis of the current program is to develop processes that are appropriate to industrial applications. It is intended to examine the potential of using a spray-drying process to produce the initial materials. One additional option is to attempt to chemisorb some of the reagents onto the active surface of a very finely divided substrate that is also the major component in the system. Hence, it may be possible to exploit the high reactivity of the substrate with the low cost of spray drying, which is well established in industry. In this manner, it should be possible to learn how far the process may be simplified and cheapened without seriously degrading the product.

One of the potential limitations of using a randomly oriented polycrystalline hydrogen conductor based on the beta-aluminas arises from their planar structure and the consequent development of significant anisotropy in many properties, including ionic conductivity. When such material is randomly oriented a number of 'blocking' grain boundaries are formed throughout the body as the highly conducting basal plane of one grain lies normal to that of its neighbour. Because the conductivity within this plane is approximately

twice that normal to the plane (6), the overall mobility of the migrating species is impeded resulting in an undesirable restriction in the power-handling capability of the electrolyte.

There are two obvious ways that this restriction can be overcome: (a) use a perfectly epitaxially oriented polycrystalline body of an anisotropic material, or (b) use isotropically (3D) conducting material in a randomly oriented body. Of these two choices, the latter is more practical because the various techniques for producing an oriented texture in the beta-aluminas all result in minimum conductivity being obtained through a thin wall or sheet - exactly opposite to what is required. Consequently, work is underway to develop and characterize materials that are reported to meet this requirement of 3D conduction.

In essence, all these materials have a structure similar to that of the zeolites; all are substituted silicates and all have been reported in the last five years. Because the first member of this group of 3D-conductors was developed as a sodium (Na) superionic conductor, it rapidly became known as 'Nasicon' (7). Within a short time, other materials were also reported to exhibit 3D conduction and because they are also superionic conductors they also became known as nasicons.

Unfortunately, this nomenclature remains confused - attempts by others to clarify the situation have not been successful. For example, the Europeans have used the basic chemical composition of the first nasicon reported (7,8) as the basis of its current name: Na-zirpsio whereas American researchers have adapted the original name to indicate that their subsequent compositions contain gadolinium or yttrium and so refer to 'Gasicon' and 'Yasicon' (9,10). Unfortunately, the field is regressing further as researchers now attempt to develop hydrogen conductors and hence reference is increasingly being made to the 'Hasicons'.

Table 1 gives the composition of the three basic materials presently under study and the research groups involved in the CANMET program. Because of the intrinsic adaptability of this technology, the present development of Na-conducting materials as precursors to possible proton conductors is also important to the development of second generation Na-conductors that may possibly replace those based on the beta-aluminas that are currently exploited by industry.

Table 1 - Basic composition of 3D-conducting electrolytes and the research groups involved

Name	Composition		Researchers
Na-Zirpsio	$Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ where $0<x>3$	(7,8)	CANMET & Queen's
	$Na_{1+x}Zr_{2-x/3}Si_xP_{3-x}O_{12-2x/3}$*	(11)	CANMET & Queen's
Gasicons	Doped-$Na_5GdSi_4O_{12}$	(9)	McMaster & Queen's
Yasicons	Doped-$Na_5YSi_4O_{12}$	(10)	McMaster & Queen's

In the last two years, some very encouraging claims have been made for the zirpsios by researchers in Germany - especially for the zirconia-deficient composition shown (*) in Table 1 (11). It has been stated that this particular family of materials is ideal for use as a sodium-conducting electrolyte in the Na-S battery and that it can also be converted to a highly conducting hydrogen conductor by a field assisted, ion-exchange process. Hence, the present focus of the CANMET program is to examine these claims. So far, it has been shown in CANMET that these materials do not occur as solid solutions as claimed but that the materials having the overall composition shown in Table 1 are always composed of free monoclinic zirconia, a sodium- and phosphorous-rich glass phase and a third crystalline phase. It is possible that the presence of a glass phase in all the compositions so far examined could limit the durability of the sintered materials in either a subsequent ion-exchange process or in service. An iterative examination of the interplay between processing, microstructure and performance will be underway in FY's 82/84.

The possibility of inadvertently creating a glass phase during the production of the chemically simpler gasicons and yasicons is reduced with the elimination of phosphorous. As these materials are known to be highly conductive to sodium, it may be possible to adapt their skeletal structure to allow high protonic conductivity. For this reason, McMaster University has been contracted to examine the variables in producing both materials, via a

spray-drying process, and to examine the possibility of producing a stable hydrogen-conducting phase from the initial sodium-conducting material. Although the work has only been underway for two months, it has already been shown that single-phase material of the highly conducting phase can be produced by this route. However, further work is required to produce a high-density sintered body before attempts can be made to ion-exchange these sintered, sodium-conducting materials.

Sodium Conductors

Interest in the field of sodium conductors and their applications stems from the pioneering work conducted by researchers at the Ford Motor company, Dearborn, who first showed that an abnormally high sodium-ion conductivity occurred in beta-alumina and that it could be exploited in a high energy-density battery based on the Na-S couple (12). Over the last 15 years since that announcement, major R & D programs have been underway to develop a commercially viable Na-S battery for use in either electric vehicles or load levelling for the utilities (13). In 1980, General Electric announced a requirement for 500,000 tubes of sodium-conducting beta"-alumina for delivery by 1985 to be used in the assembly of probably a 0.5-MWh Na-S battery as part of the BEST (Battery Energy Storage Test) facility operated by the Electric Power Research Institute for the Department of Energy in the United States (14). Since 1980, Ford has been testing 50-kWh units.

During the past eight years, researchers have succeeded in developing high-quality beta-alumina and the more conductive beta"-alumina. In practice, additives such as lithia (favoured in the United States) and magnesia (favoured in Europe) have been found helpful in promoting the normally sluggish formation of the beta"-phase. As a result, the resistivity of the early beta-materials has been reduced by a factor of approximately five as the beta" compositions were developed and the processes improved.

Although such materials have been demonstrated by Ford in Na-S cells that have operated for over 8000 charge-discharge cycles, the question of electrolyte durability, especially at high current density, has been raised in recent years. Members of the Ford Research group were the first to show that sodium dendrites can be formed in the bulk of the electrolyte and these can lead to the catastrophic failure of a battery. It was postulated that an ion-current focussing mechanism was created around internal cracks and these

resulted in the rapid deposition of an excessive quantity of sodium locally at or near to a crack tip. At high current density, when the rate of deposition of the sodium exceeded its rate of removal from the tip, an internal Poiseuille pressure was rapidly generated, which extended the crack, leading to failure.

If this mechanism were correct, it was postulated that the durability of the electrolyte should be extended by the application of an external compressive stress - the level of mechanical stress for extended lifetimes being perhaps related to the overall current density. If this were so, it was clear that the durability of the electrolyte in service could be simply extended by system design. Hence, a contract was let to McMaster University under NRC funding to examine the effect of both tension and compression in four-point bend made on notched bars of sodium beta"-alumina that were also the electrolyte in a concentration cell undergoing charge-discharge cycles. Contrary to expectation, the electrolyte degraded equally under both tension and compression suggesting that stress corrosion and not Poiseuille pressure is the dominant failure mechanism. This work is continuing.

Industrial Development of Sodium Beta"-alumina

The transfer of the seed technology for the production of high-quality sodium beta"-alumina to Almax Industries Ltd. was mentioned above. This transfer arose from a 32-month development program conducted by the company with sub-contracted researchers at the Ontario Research Foundation to demonstrate a novel thermo-electric generator. This work, which was started in early 1979 and completed in late 1981, required the company to develop three sodium-conducting solid electrolytes, to design, fabricate and commission a thermo-electric generator and to demonstrate the operation of the generator using their own electrolytes. In the event they produced two generators: one based on a flat-plate and one based on a closed-ended tube design. This allowed the non-recirculating flat-plate type to be used for screening the wide range of compositions that were studied in the program and the optimized materials that were so identified were then used in the recirculating closed-ended type for demonstration purposes.

As a result of this program the company was in a position at the end of 1981 to produce 1-kg batches of powder that can be sintered into high-quality tubes or plates of beta"-alumina having a total resistivity of ~5

$(ohm.cm)^{-1}$ at 575 K. As the size of a normal production batch of specialty ceramic powders is 200 to 300 kg, it can be appreciated that an increase of just over two orders of magnitude in the batch size will require further development. In addition, the durability of the product will require demonstration under operating conditions that include long-term contact with liquid sodium at temperatures up to 1000 K. These objectives form part of the requirement of a PILP-supported program, operated by the National Research Council through Energy, Mines and Resources Canada, in which the company is required to engineer and demonstrate the operation of a thermo-electric generator that will produce electric power using the waste heat released from the company's production furnaces. This will probably also involve the use of high-temperature heat-pipe technology. The program is scheduled for completion in 1985.

Devitrification of Glass

One of the common limitations of producing polycrystalline solid electrolytes is the practical difficulty of developing theoretically dense material of the desired grain size and final composition. Frequently, a compromise has to be struck between using a high sintering temperature that will develop high density, strength and conductivity (but which will also lead to the preferential loss of some of the more volatile components from the system) and the use of a lower sintering temperature that will reduce the problem of selective volatilization (but will usually result in a lower-density product).

It was with these thoughts in mind, coupled with the fact that the 3D conductors have a liquidus point in the temperature range from ~1300 K to 1650 K (compared with over 1875 K for the 2D-conducting beta-aluminas), that researchers at McMaster University suggested the possibility of forming these materials by rapidly melting and using standard glass-forming techniques followed by a lower temperature annealing cycle to devitrify the material, thereby forming a fully dense, crystalline product having the required geometry. The devitrification stage was thought necessary because glasses typically have an ionic conductivity ~1000 times less than that of a crystalline material.

The idea was appealing and hence work in this area was commenced at McMaster in mid-1981 to examine the possibility of producing crystalline gasicons and yasicons via a glassy phase. Unfortunately, the process was soon

shown to be impractical - surprisingly, it was found that the crystalline phases have a higher specific volume than the glass phase and this resulted in cracking during the devitrificaiton stage. In addition, the body did not fully devitrify but retained ~5% of the glassy phase at the grain boundaries. The work was terminated after six months.

Non-destructive Evaluation

One of the concerns facing both the producers and users of most solid materials is to ensure that the quality meets certain specifications prior to its use in an assembly. In the case of polycrystalline sintered materials that have to withstand certain mechanical and electrical stresses, the assurance that sub-surface defects are absent is important. For this reason, the CANMET program has a component to develop suitable techniques that will be able to detect five-micrometre defects in material having a thickness of ~1 mm.

Present techniques only allow the detection of sub-surface defects of ~75 micrometres using commercially available ultrasonic equipment. Consequently, emphasis is being placed on the development of transducers, automatic scanning systems and acoustic signature analysis of defects that have been intentionally introduced as either voids or inclusions in both glasses and crystalline ceramics.

So far, voids down to ~30 micrometres have been detected but indications are that to locate much smaller defects it is necessary to design and build transducers that cover the frequency range from 75 to 400 MHz and which have a so-called 'screw-driver' beam in which a parallel beam is emitted by the device instead of the more common focussed beam from a hemispherical transducer. In this way, it is anticipated that an XY scan of a surface with such a beam will also give a full scan in the Z direction (into the material). The currently available focused transducers make it necessary to make repeated XY scans of the same surface using different Z distances between the transducer and the material in order to build up a picture of the internal defects in the XYZ volume.

If successful, this work will have important applications in the quality control of a wide range of materials, not just solid electrolytes. This program is continuing.

Conductivity Determination

Another aspect of electrolyte quality control that will have to be addressed in a production environment is the ability to rapidly measure the conductivity of closed-ended tubes in order to be sure that the product meets its specifications. In a research environment, this is universally done using a direct method and contacting electrodes. However, that would be impractical on a production line and so effort is also being devoted to the development of a non-contacting and rapid method for measuring the conductivity (or a related parameter) that is suitable for use on a production line.

In March 1982, a contract was completed by researchers at Queen's University to determine if any correlation existed between conductivity of sodium-conducting electrolytes and the nuclear magnetic resonance (NMR) spectra. Although a series of correlations was found, it would clearly be impractical to use standard NMR techniques as the non-contacting method because the capital investment for a 4-5 Tesla magnet and associated electronics would be prohibitive. However, although the contract was not intended to examine the aspect of non-contacting conductivity measurements, it did suggest that the use of a balanced RF bridge could be developed that would be suitable.

In essence, i' is expected that by inserting an electrolyte tube into one side of a bridge, the degree of imbalance will be related to the conductivity. In this manner, it should be possible to quite rapidly scan down the length of a tube for changes in conductivity that might result from microstructural or compositional variations. One of the attractive aspects of this approach is that the technique should be capable of operation by unskilled labour. This program is continuing.

FUTURE R & D

At present, the CANMET program is in a state of transition: the technology for producing the sodium-conducting beta-aluminas has been transferred to industry, which is in the process of scaling up the production facilities, while the exploitation of hydrogen conductors is only in its infancy in the laboratory.

Because of the potential of 3D sodium conductors to displace the beta-aluminas in the future in various energy-related applications, work is

planned to examine those materials shown in Table 1. This will include developing optimized processing for each material and determining its performance in small-scale devices. The work with the 3D sodium conductors is of particular interest because of the possibility of producing 3D proton conductors. It is intended to examine this aspect during the course of the program.

At present, the 2D proton conductors based on the beta-aluminas are produced using a freeze-drying technique, which is slow and hence unsuitable for industrial needs. It is intended to parallel this work (which results in high-quality materials) with a study on the use of spray drying to produce the proton-conducting precursor thereby attempting to exploit the cheaper processing that results from spray drying without greatly compromising the properties of the product. It is hoped that satisfactory materials will be prepared by drying aqueous slurries in which either the minor reagents are in solution or adsorbed onto the surface of the major reagent.

An additional area of R & D that can be anticipated for any device that exploits the proton conductors is the development of suitable electrodes. At first, noble materials will be used in order to determine the durability of the materials under operating conditions. In addition, work will also be devoted to producing, characterizing and using both non-noble metals and ceramics as potentially useful lower-cost electrode materials. It is anticipated that this phase of the work will be completed by 1985. Thereafter, the first working cells will be constructed based on some of the preliminary cell work that is planned for 1984.

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